Energy Transfer in Competition to Charge Transfer as a Method to Determine the Rate Constant for Charge Carrier Injection in the Sandwich System: Cyanine Dye Monolayer/p-Chloranil Crystal *

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A new method is described to calculate the rate constant for charge transfer (CT) from an excited dye to a molecular crystal by taking into account competing energy transfer to a metal electrode. For the system oxacarbocyanine dye/p-chloranil single crystal in a sandwich arrangement with additional arachidic acid monolayers and evaporated aluminium electrodes, based on photocurrent and fluorescence measurements $k_{\mathrm{CT}} = (1.5 \pm 0.7) 10^9\ \mathrm{sec}^{-1}$ has been calculated.

This overall rate constant is discussed in terms of a detailed but simple reaction scheme for charge carrier injection. It turned out to be equal to the dissociation rate constant of the excited dye times the quantum efficiency Φ_{CT} for dissociation of an intermediate "charge transfer" state. Dissociation occurs from a vibrationally relaxed excited state of the dye.

Finally, comparison is made with a straightforward calculation using the well-known unipolar current density. Nearly quantitative agreement of estimations emphasizes the use of the monolayer technique to build "dry" electrochemical cells in order to study the principles of photoelectrochemical reactions.

1. Introduction

Energy transfer and charge transfer have for a long time been considered to be competing models for the description of the sensitizing action of dye molecules on the surface of silver halides [1]. Moreover, regarding the results for energy transfer [2] and taking into account potential considerations about electron transfer [3], West [1] has pointed out that, provided the energetic requirements for energy transfer as well as for electron transfer are met, electron transfer could probably compete with energy transfer. A distinction between both processes should depend on the regeneration process and not be possible if this is a fast process [1]. More recently, charge transfer from excited dye molecules into a silver halide crystal has been proved directly by electrochemical techniques [4a, b].

Charge carrier injection from excited states into molecular crystals has been studied since the pioneering work about iodine decay [5] and the decay of excited dyes [6] at the phase boundary of molecular crystals. Although the energetic requirements of the reaction mechanism are rather well understood now and can be interpreted as electrochemical reactions at electrodes of insulating material [4a] it is very difficult to obtain reliable results about reaction rates. In principle, and if there are no competing reaction paths, a rate constant k_{CT} can be determined from an unipolar, electrode-limited current density

$$j = e\, k_{\mathrm{CT}} [D^*]\,, \tag{1}$$

where e is the electronic charge and $[D^*]$ the surface density of excited dye molecules D^*.

But usually it is the determination of the surface density $[D^*]$ that limits severely the applicability of this equation. This holds mainly for crystal/solution interfaces because of the competing adsorption of solvent and dye molecules and the formation of dimers and aggregates. Even with inorganic substrates only a few cases can be described by simple adsorption kinetics [7]. Moreover, adsorption may influence the decay time of excited molecules [8a, b], and therefore the calculation of the density of excited states is not unambiguous if data from measurements with the dye in solution are used.

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The use of monolayers avoids adsorption problems. The amount of adsorbed dye molecules on the crystal surface can be controlled by comparison with the absorbance of a layer with the same composition on a glass slide. Those "dry" electrochemical cells with evaporated aluminum electrodes, like

aluminum/crystal/dye, arachidic acid/aluminum

have a onedimensional geometry perpendicular to the phase boundary. The rigid structure in the sandwich arrangement prevents the decomposition of dye molecules and makes possible stable photocurrents for a long period.

With these arrangements it has been shown that energy transfer from the excited dye at the crystal surface to the adjacent metal competes with charge transfer to the crystal and yields decreasing photocurrents with decreasing distance of the evaporated electrode from the adsorbed dye [9]. From absolute ratios of quenched to not quenched current densities a rate constant for charge carrier injection from an oxacarbocyanine dye into p-chloranil crystals has been reported to be $k_{\mathrm{CT}} = (4 \pm 2) \times 10^8\ \mathrm{s}^{-1}$.

The present paper reports on a new way to determine the rate constant without simplifying assumptions. In addition to the previously reported results about photocurrent measurements, fluorescence measurements of the distance dependent quenching of the oxacarbocyanine dye were necessary and have been made [10]. The rate constant is now $k_{\mathrm{CT}} = (1.5 \pm 0.7) \cdot 10^9\ \mathrm{sec}^{-1}$.

It is discussed in terms of an electrode limited, unipolar current density of a heterogeneous charge transfer reaction, based on a simple reaction scheme that is also developed.

2. Experimental

The preparation of the measuring cells for the photocurrent measurements has partially been described elsewhere [9, 11]. In more detail, the sandwich arrangements have been built in several steps (Figure 1). At first, one electrode of aluminum is evaporated in vacuo onto one of the (*a*, *b*)-surfaces of the p-chloranil single crystals that have been grown by sublimation [12] in flakes of about 0.5 cm² area. Afterwards a mixed monolayer of the dye 3,3′-distearyl-oxacarbocyanine chlorate [13] and of arachidic acid with a mole ratio of 1:20 has been deposited by monolayer techniques [14]. The surface pressure was 40 dyn/cm. Additional monolayers of pure arachidic acid yielded increasing distances in steps of 27 Å between the monolayer of the chromophore at the very surface of the crystal and the second evaporated aluminum electrode. In addition to the dye with a stearyl chain of 25 Å, up to 4 monolayers have been inserted by this way as spacers. The electrodes were deposited by evaporation of aluminum from a boat source in a vacuum of about $5 \cdot 10^{-5}$ mbar (Figure 1). The crystals were placed on a masc with holes of 4 mm diameter that was in thermal contact with a vessel that was cooled by liquid nitrogen. By the cooling, the vacuum was also improved, which reduced the evaporation time. Thus, together with the cooling of the sample, less damage of the dye molecules by the intense IR radiation from the heated boat occurred. In addition, the latter was partially covered by a radiation shield [15a].

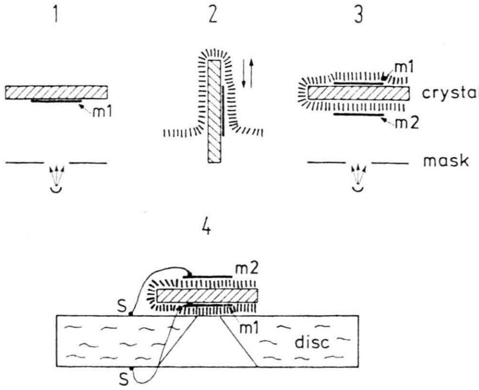

Fig. 1. Procedure for sandwich cell preparation with crystals.

1) aluminum deposition m1 by evaporation through a mask;
2) Monolayer deposition by dipping technique [14, 15];
3) deposition of the second semitransparent metal electrode m2;
4) mounting with grease onto a disc of plastics (PVC); electrical connexions with silver paste (s).

The electrodes had a typical transparency of about 20% that was controlled during evaporation by an optical detector behind a simultaneously evaporated glass slide [15b]. The absorbance of this glass slide was measured afterwards in a spectrometer. A set of probes with 1 to 5 layers has always been prepared simultaneously in order to avoid differences of the sandwich cells as regards vacuum, duration of evaporation and, thus, transparency of the electrodes as well as density of dye molecules on the surface [15a].

The crystals were mounted onto a support of plastics as shown in Fig. 1, 4, and electrical contact to the electrodes was made with lines of silver paste.

These lines have to be thin in order to reduce dark injection. The disc of plastics was afterwards mounted into a measuring chamber with quartz windows and electrical connections. Photocurrent measurements have been made with the measuring arrangement shown in Figure 2. The dye covered surface of the crystal is illuminated by a tungsten lamp through a motor-driven monochromator. If the illuminated electrode is negatively biased by a high voltage supply (typically about 100 volts) a wavelength dependent photocurrent can be measured with an electrometer that has a sensitivity up to 10^{-14} amps. The spectra have been recorded with an x-y-recorder. Current-voltage characteristics and intensity dependencies have been measured by using the 496 nm line of an argon ion laser as a source of constant and calibrated light intensity.

The preparation of probes for the optical detection of fluorescence and absorbance has been described in detail elsewhere [14a, b] in connection with the broad application of monolayers for the study of organized systems. For the present investigations glass slides of size 1×4 cm were coated from one side with vacuum deposited aluminum, the transparency of which was again about 20% and thus comparable to that of the electrodes of the sandwich cells. Afterwards, the dye monolayer with the same mole ratio 1:20 as above was deposited and then coated with two monolayers of pure arachidic acid. Additional monolayers of inert arachidic acid between the dye layer and the metal surface, respectively, yielded an increasing distance in steps of 27 Å of the chromophore from the energy quenching metal.

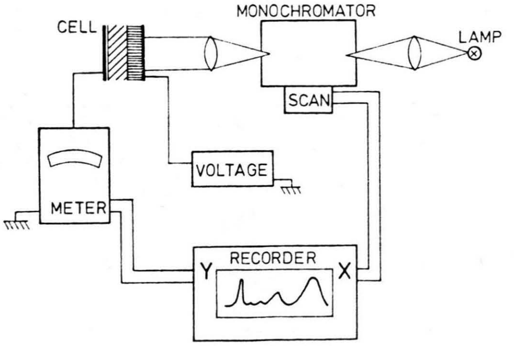

Fig. 2. Measuring equipment: That side is illuminated where the monolayers are undisturbed between the crystal and the metal electrode.

It should be noted that the monolayer assemblies covered the glass slides on both sides. Whereas the side with the evaporated aluminum layer was used for measurements of the distance dependent fluorescence quenching, the other side was used as a reference to yield the fluorescence intensity of unquenched dye molecules.

The fluorescence measurements have been done with an apparatus that has been designed especially for the detection of the weak intensities that are conditioned by a monolayer [16]. The dye has been excited by the intense band of a mercury lamp at 435.8 nm.

3. Measurements and Results

3.1. Fluorescence Measurements

The fluorescence decay time of an excited dye at a distance $d \leqq 500$ Å in front of a metal decreases with decreasing distance from the surface. The phenomenon has been treated quantitatively by Kuhn [17] by considering energy transfer from an emitter molecule to an acceptor by calculating the average rate of energy absorption of a thin absorbing layer from an electric dipole emitter at a distance d. With the field component oscillating in the plane of the layer and in the proximity field approximation for distances that are small compared to the wavelength of the excited dye, $d \ll \lambda$, a simple relation has been obtained

$$q(d)/q(\infty) = \tau(d)/\tau_F = 1/[1 + (d_0/d)^4]. \quad (2)$$

The ratio of the fluorescence quantum yields of a molecule at distance d to that of a molecule at infinite distance from an absorber, $q(d)/q(\infty)$, is equal to the ratio of the relevant decay times $\tau(d)/\tau_F$ (τ_F is the fluorescence decay time in the absence of an acceptor), if there is only a weak perturbation of the radiation field of the emitter by the absorber. This holds for not ideal metal mirrors where the induced dipole is much smaller than the emitter dipole [17]. The parameter d_0 can be determined experimentally.

The present fluorescence measurements have been obtained by exciting with the mercury line at 435.8 nm oxacarbocyanine dye monolayers with a mole ratio of 1:20 on evaporated films of aluminum with a typical transparency of 20%. The spectra have not been corrected for constant fluorescence intensity, because afterwards only their ratios were used. But comparison with fluorescence standards shows that in this wavelength region no substantial deviations occur.

The fluorescence spectra for a typical sample with the dye layer at a distance $d = 108$ Å from the aluminum as well as for a dye layer on a glass slide without a metal layer ($d = \infty$) are shown in Figure 3. They reveal 3 bands at 510, 540 and 575 nm. Earlier, bands at 510 nm and 580 nm have been found and ascribed to monomer and dimer fluorescence, respectively [15]. But it should not be excluded that the broad band at 575 nm is due to phosphorescence, because the rigid structure due to adsorption favours, like cooling, luminescent transitions from the triplet state [8b]. In this case the band at 540 nm could be ascribed to dimer fluorescence.

The dependence of the fluorescence intensities of the oxacarbocyanine dye on the distance in front of the evaporated aluminum layer, and normalized to the not quenched fluorescence intensity, is plotted in Figure 4. The scatter of the values for different probes is indicated by the open bars. Nevertheless, they follow with sufficient accuracy a plot of (2) with the experimentally determined $d_0 = (99 \pm 6)$ Å at the ratio $q(d)/q(\infty) = 1/2$.

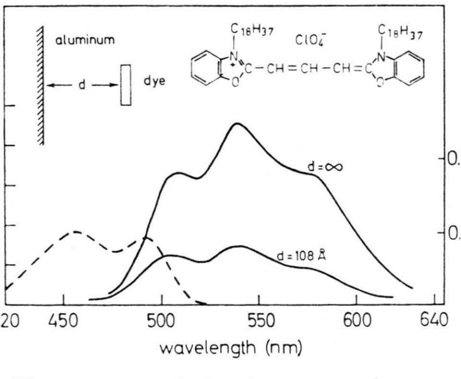

Fig. 3. Fluorescence and absorbance of a dye monolayer with mole ratio 1:20 on a glass slide; left scale: fluorescence measurements (——) at different distances from the metal layer with peaks at 510, 540 and 575 nm; right scale: absorption measurements (- - -) with peaks at 460 and 496 nm. Details see text.

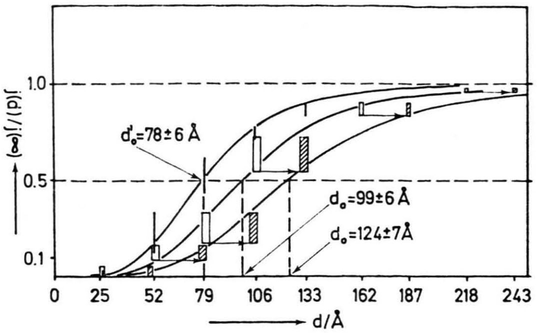

Fig. 4. Ratios for fluorescence (open and dashed bars) and photocurrent measurements (black bars). The curves have been calculated with the inscribed parameters, $d_0' = (99 + 25 = 124)$ Å is obtained under the consideration of an additional spacer of Al_2O_3 with 25 Å (arrows).

The functional dependence of (2) has been found in many monolayer assemblies with dye layers [14a, b], but also with a dye monolayer that has been deposited at well defined distances on thin gold layers [18]. The present measurements show deviations with respect to the fit of (2) in Fig. 4, and especially in a logarithmic plot, where straight lines with slope 4 should be observed (Figure 5). They can be explained by experimental conditions and physical reasons:

The evaporated aluminum films with a thickness of about 120 Å [15b] can be uneven. Moreover, before depositing the monolayers, the aluminum covered glass slides were handled in air for some hours. During this time a film of Al_2O_3 with a thickness of about 25 Å could have formed [19]. This would be an additional spacer between the dye and the energy quenching metal. Its influence on d_0 depends not only on its thickness but also on its homogeneity and its dielectric constant.

Quantitatively, there is no exact knowledge about these quantities, but qualitatively it can be seen from Fig. 4 that with the assumption of an additional spacer of 25 Å, a plot with a parameter $d_0 = (99 + 25) = 124$ Å fits also the present results, although with less accuracy. An even better fit is obtained with $d_0 = 124$ Å in the logarithmic plots in Fig. 5, that are derived from (2) for the ratio of intensities I by

$$\frac{q(\infty)}{q(d)} - 1 = \frac{I(\infty)}{I(d)} - 1 = \frac{d_0^4}{d^4}. \qquad (2a)$$

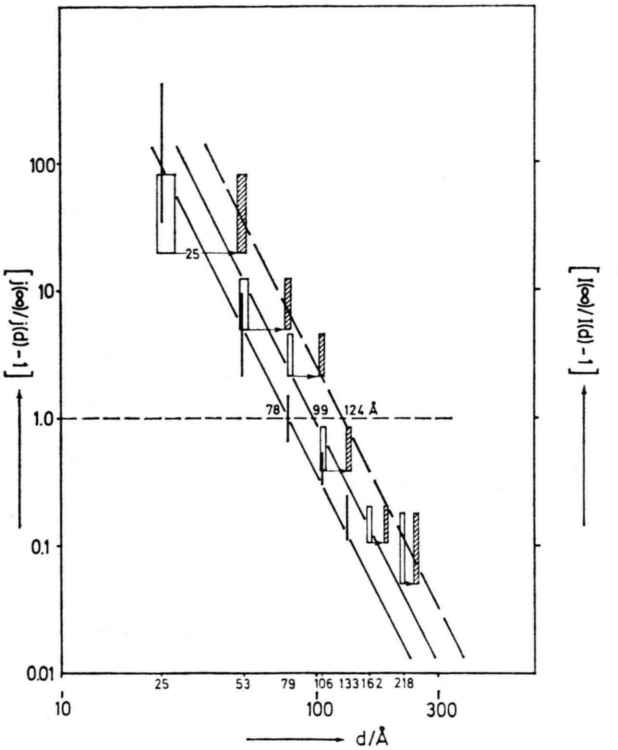

Fig. 5. Logarithmic plot of the measurements that are given in Figure 4. The straight lines with slope 4 have to go through the intercept at d_0 and d_0', respectively, where $[j(\infty)/j(d_0')-1]=1$ (the same holds for the fluorescence measurements). The arrows indicate the additional distance of 25 Å.

The straight lines with slope 4 have to go through the intercepts d_0 at $[I(\infty)/I(d)-1]=1$.

Nevertheless, the value of these parameters should not be overestimated because the bars at small distances have a large scatter due to experimental reasons, and those at larger distances have an increasing error because $I(\infty)/I(d) \approx 1$. But these uncertainties affect neither the principles of the method nor severely the value of the rate constant (Sect. 3.3). Therefore it seems to be reasonable to decide for $d_0 = 99$ Å on the basis of an idealized concept.

The situation is quite different in case of the sandwich cells with $d_0' = 78$ Å, where the evaporated aluminum electrode covers the monolayer assembly and oxygen access affects mainly the not quenching active outer electrode surface. Therefore, between the crystal surface and the aluminum electrode the distance is given by the number of monolayers.

Instead of the d^4-dependence of (2) a d^3-dependence has been suggested to describe the nonradiative energy transfer rate constant for an oscillating dipole at small distances $d \leqq 500$ Å in front of a thick metal layer [20], and experimental evidence has been given apparently for fluorescence decay of singlet excitons at aluminum and gold electrodes on the surface of anthracene crystals [21a—c]. But, apart from the physical fact that induced charge densities have only a small, frequency dependent penetration depth (skin effect) the application of point dipole models in front of dielectric media should fail where the extension of the dipole in the dye molecule is comparable with its distance from the surface. Moreover, in the experiments described above [21a—c] the emitter is not restricted to a plane but is extended into the bulk of the crystal. Thus, integration over the exciton density inside the crystal is necessary as it has been indicated, although not carried out, by Kallmann et al. [21c].

Vice versa, the experimental results given by Baessler et al. [21a—c] correspond to integrated fluorescence intensities, and differentiation yields the d^2-dependence of a quasi-linear problem. Although not recognized by the authors, these exact measurements are an example for a cooperative energy transfer process. It is similar to the energy transfer from aggregates as treated by Kuhn [17], where opposite charges of the dipoles along a chain compensate each other. The regular and oriented arrangement of anthracene molecules in the lattice plane favours the cooperative in phase oscillation, especially when excited with polarized light. The density of excited states in a molecular plane might, therefore, play an important role in the transition from a d^2- to a d^4-dependence of the fluorescence quenching, that has hitherto nowhere been considered.

In phase oscillations are not possible in the random distribution of dye molecules in a monolayer. But if there exists a preferred orientation, an experimentally determined slope should be more justified than the theoretical d^4-law. Because of the large error bars, this has not been taken into consideration in the present treatment.

3.2. *Photocurrent Measurements*

Photocurrent measurements have been made with the sandwich systems (Fig. 2). The action

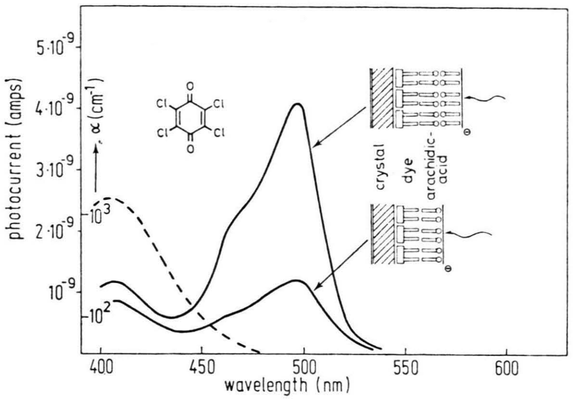

Fig. 6. Typical photocurrent measurements (——) with different distances of the dye from the aluminium electrode as indicated. The absorbance of a p-chloranil single crystal is also shown (– – –, inner scale). The curves are normalized to constant light intensity.

spectra that have been obtained by illumination of the negatively biased, dye covered surface with monochromatic light, show maxima at 408 and 496 nm, and a shoulder at 465 nm (Fig. 6).

The peak at 408 nm is due to the dissociation of triplet excitons at the phase boundary. They are generated by excitation of n-π^* singlet excitons (2.7 eV) within the crystal bulk (Fig. 7, left side). Within experimental accuracy it can be stated that only for distances $d < 54$ Å it decreases slightly with decreasing d. This proves not only that energy transfer from triplet excitons to the metal is not an efficient process because it is a short ranged exchange interaction of Dexter type [23], but implies also that dissociation of an excited surface molecule ^{3}CA* occurs rather at the directly adsorbed dye (D) or the carboxylic groups of arachidic acid (A) molecules, yielding an electron e^-_{CA} within the crystal,

$$ {}^3CA^* + D, A \xrightarrow{k_{ex,CT}} e^-_{CA} + D^+, A^+ , \tag{3}$$

than at the metal electrode where for a distance of 27 Å an efficiency of only 10^{-2} has been found [24].

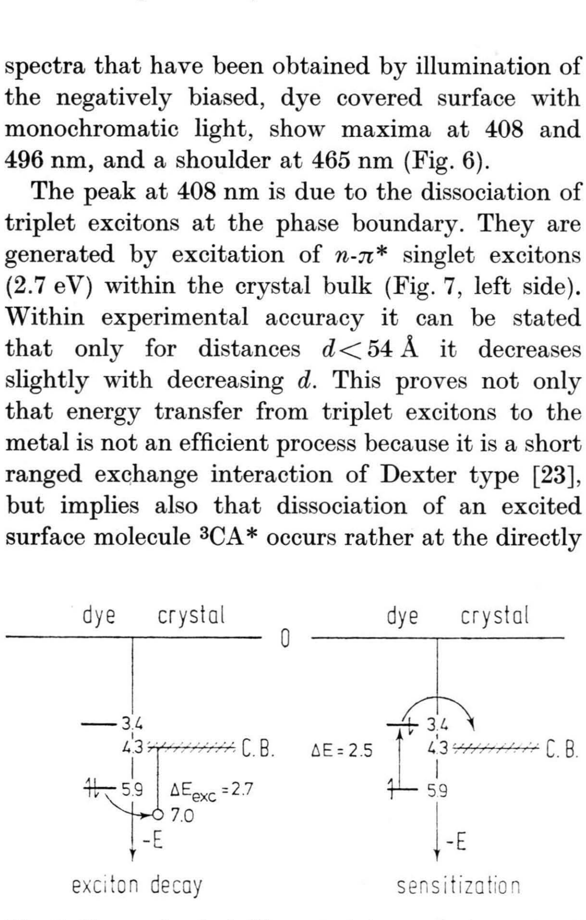

Fig. 7. Energy levels (with respect to an electron at rest in vacuo) that are relevant for exciton decay (left side) and sensitization (right side). An n-π^* singlet exciton is indicated (2.7 eV) from where a triplet with 2.39 eV is formed. The dashed area of C.B. means not the width of the conduction band but the uncertainty of its location.

The peak at 495 nm with a shoulder at 465 nm resembles the absorbance of a dye monolayer on a glass sliee (Fig. 3 compared to Fig. 6) [15a]. It comes from the sensitizing action with a charge transfer rate constant k_{CT} of the excited dye D^* with a surface density $[D^*]$ (Fig. 7, right side)

$$ D^* + CA \xrightarrow{k_{CT}} D^+ + e^-_{CA} . \tag{4}$$

With light intensity I and an absorption cross section $\sigma(\lambda)$ the photocurrent density becomes

$$ j = e\,\sigma(\lambda)\, I [D]\, \Phi_{CT}(d) . \tag{5}$$

It decreases via the quantum efficiency for charge transfer, $\Phi_{CT}(d)$, with decreasing distance of the adjacent evaporated metal electrode from the dye molecules on the crystal surface.

Several sets of probes as described above (Sect. 2) have been measured and the scatter of values is indicated by the bars in Figure 4. The dependence of the ratios of quenched to unquenched photocurrents or quantum efficiencies, respectively, on the distance d,

$$ \frac{j(d)}{j(\infty)} = \frac{\Phi(d)}{\Phi(\infty)} = \frac{1}{1 + (d_0'/d)^4} , \tag{6}$$

with the experimentally determined parameter $d_0' = 78 \pm 6$ Å at $\Phi_{CT}(d_0')/\Phi_{CT}(\infty) = 1/2$, is similar to (2) and deduced in the following section.

In contrast to the fluorescence measurements, where $q(\infty)$ is simply obtained by the fluorescence of a monolayer on a glass slide, the photocurrent measurements are available only up to a distance of 133 Å between the dye and the metal electrode. Therefore, for each set of probes with distances up to 5 monolayers, the values $j = j(d)$ have been plotted and, using also $\Phi_{CT}(d_0)/\Phi_{CT}(\infty) = 1/2$ at the turning point, an extrapolation to $\Phi_{CT}(\infty)/\Phi_{CT}(\infty) = 1$ has been performed graphically.

The same bars as in Fig. 4, plotted in the logarithmic scale of Fig. 5 allow for a straight line through $d_0' = 78$ Å with a slope 4. The deviations at larger distances are smaller than those in an earlier plot [9] with slope 3.8, that holds for $d < d_0'$.

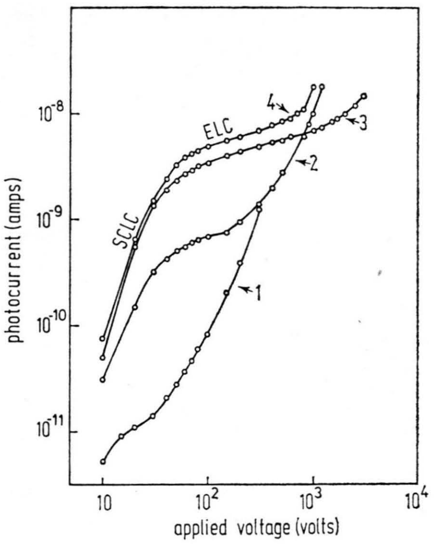

Fig. 8. Current-voltage plots of one set of probes that has been prepared simultaneously. The labels indicate the number of monolayers between the crystal surface and the adjacent metal electrode; the first monolayer contains the dye. Excited at 496 nm.

Photocurrent densities depend on the applied voltage. In agreement with injection currents into molecular crystals [25], typical current-voltage plots (Fig. 8) start with a space charge limited region and proceed at higher field strengths of about 10^4 V cm^{-1} with a transition into an electrode limited current (ELC). The latter follows for an extended voltage range a plot $j \sim \exp(bE^{1/2})$; b is the Schottky constant [26] and can be derived from the well-known Butler-Volmer relation [26d].

Figure 8 shows current voltage plots for a set of sandwich cells with increasing distances from 25 Å to 106 Å between the dye and the adjacent metal layer. Unfortunately, not every cell works because of known or unknown mistakes during preparation and handling. Therefore, no complete set with distances from 25 to 133 Å can be presented. But Fig. 8 is a good and typical example to show the increasing range of the ELC with increasing distance of the excited dye from the metal. The steeper increase at the end of the curves has a relation to the dark current behaviour that increases also in this voltage range.

The wavelength dependent photocurrents and the values in Fig. 4 were recorded with a voltage just beyond the space charge limited region, i.e. with 100 volts. It can be seen that this value is too high for the curve at smallest distance where the ionized dye molecules cause an additional internal field induced current from the metal [27].

Finally, intensity dependent measurements (Fig. 9) with intermittent irradiation by the 496 nm line of an argon ion laser for about 4 seconds show for each point a nearly linear relationship (slope 0.9 in Fig. 8) between photocurrent and light intensity up to illumination rates that are far higher than those used in the distance dependent measurements. These have been made in the range from 100 to 500 μW cm^{-2}. An earlier reported square root dependence [9] turned out to be an artifact that came in by a misinterpretation of photocurrents that were decreasing due to a possible destruction of the cells under steady state illumination with high intensities larger than 1 mW cm^{-2}.

Together with high quantum efficiencies ($\Phi_{CT} \leqq 1$) and the electrode limited voltage dependence this linear intensity dependence assertaines that not the regeneration of the dye causes saturation effects with increasing number of inserted layers of arachidic acid. Indeed, the regeneration of dye molecules occurs via the layer system and is thus clearly localized. It is possible because the ionized dye molecules cause a high electric field larger than 10^6 V cm^{-1} between the dye and the metal electrode, which has been assertained independently by the electrochromism of a merocyanine dye [28]. The conductivity of arachidic acid monolayers between

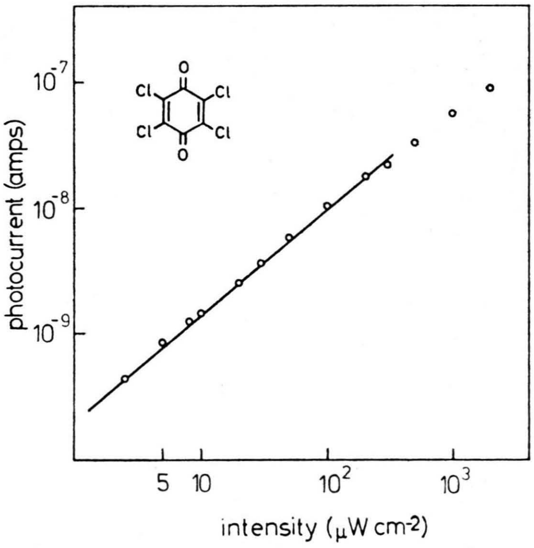

Fig. 9. Current-intensity relationship; slope 0.9 has been evaluated. Excitation occurred with intermittent light of the 496 nm line of an argon ion laser.

metal electrodes has been measured [29]. It allowed for current densities up to 10^{-6} amps cm^{-2}. The rather good conductivity of monolayer assemblies can be explained by conductivity tunnelling [30a] or a model of quantum mechanical hopping [30b].

3.3. Evaluation of the Rate Constant k_{CT}

The dye is directly adsorbed on the surface of the p-chloranil single crystal. If we neglect internal deactivation processes for those dyes with a high fluorescence efficiency, the decay time of the excited state $\tau(d)$ is now determined by the rate constants of three decay channels, i.e. fluorescence, k_{F}, energy transfer to the metal, $k_{\mathrm{ET}}(d)$, and charge transfer to the crystal, k_{CT}:

$$\tau(d)=\frac{1}{k_{\mathrm{CT}}+k_{\mathrm{F}}+k_{\mathrm{ET}}(d)}\,. \tag{7}$$

It depends thus also on the distance of the dye from the metal surface via $k_{\mathrm{ET}}(d)$.

Therefore, the quantum efficiency $\Phi_{\mathrm{CT}}(d)$ in (5), that depends on the ratio of the rate constant for charge transfer k_{CT} devided by the rate constants of all deactivation processes that are considered in (7), becomes

$$\Phi_{\mathrm{CT}}(d)=\frac{k_{\mathrm{CT}}}{k_{\mathrm{CT}}+k_{\mathrm{F}}+k_{\mathrm{ET}}(d)}\,. \tag{8}$$

If the rate constants for fluorescence and energy transfer are drawn together to a distance dependent rate constant for the decay of the excited dye when there would be no competing charge transfer to the crystal, $k_{\mathrm{F}}+k_{\mathrm{ET}}(d)=k(d)$, this second term in (8) can be replaced by (2) for lifetime shortening by energy transfer,

$$k(d)=k_{\mathrm{F}}[1+(d_0/d)^4]\,, \tag{9}$$

and the distance dependent quantum efficiency for the sensitized photocurrent becomes now

$$\Phi_{\mathrm{CT}}(d)=\frac{1}{\dfrac{k_{\mathrm{CT}}+k_{\mathrm{F}}}{k_{\mathrm{CT}}}\left[1+\dfrac{k_{\mathrm{F}}}{k_{\mathrm{CT}}+k_{\mathrm{F}}}\left(\dfrac{d_0}{d}\right)^4\right]}\,. \tag{10}$$

Normalization to unquenched photocurrents, where $d=\infty$, yields after some rearrangement

$$\frac{\Phi_{\mathrm{CT}}(d)}{\Phi_{\mathrm{CT}}(\infty)}=\frac{1}{\left[1+\dfrac{k_{\mathrm{F}}}{k_{\mathrm{F}}+k_{\mathrm{CT}}}\left(\dfrac{d_0}{d}\right)^4\right]}\,. \tag{11}$$

The evaluation of the rate constant for the charge transfer step is now possible in an analytical way [10] if the parameter d_0' is introduced for the photocurrent measurements,

$$(d_0')^4=\frac{k_{\mathrm{F}}}{k_{\mathrm{F}}+k_{\mathrm{CT}}}(d_0)^4\,. \tag{12}$$

The insertion of (12) into (11),

$$\frac{\Phi_{\mathrm{CT}}(d)}{\Phi_{\mathrm{CT}}(\infty)}=\frac{1}{1+(d_0'/d)^4}\,, \tag{13}$$

shows the similarity of the dependences on the distance of the ratios of photocurrent (13) and fluorescence (2) efficiencies. That is, despite the fact that we are measuring the photocurrent efficiency, we get the functional dependence of fluorescence quenching (Figure 4).

Whereas $d_0=(99\pm6)$ Å can be determined from optical measurements, $d_0'=(78\pm6)$ Å can be determined from photocurrent measurements. The insertion of these values into

$$k_{\mathrm{CT}}=k_{\mathrm{F}}[(d_0/d_0')^4-1] \tag{14}$$

yields, with $k_{\mathrm{F}}=9.1\cdot10^8\ \mathrm{sec}^{-1}$ for the decay constant of the fluorescence of dye molecules in a monolayer [31], the rate constant for the sensitized charge carrier injection into the p-chloranil crystal

$$k_{\mathrm{CT}}=(1.5\pm0.7)\cdot10^9\ \mathrm{sec}^{-1}\,.$$

The error is given by experimental incertainties in the determination of d_0 and d_0' from Figure 4. Equation (14) shows that the method is the more pronounced the more d_0 and d_0' differ from each other. The condition $d_0>d_0'$ is physically reasonable for all systems with charge transfer interaction.

The formation of the $\mathrm{Al_2O_3}$-layer with a thickness of up to 25 Å as described before would act as an additional spacer. In this case, $d_0=124$ Å and (14) yields $k_{\mathrm{CT}}=5\cdot10^9\ \mathrm{s}^{-1}$. This value would be even closer to an earlier estimation [11a] of $k_{\mathrm{CT}}\approx10^{10}\,\mathrm{s}^{-1}$, and the rate constant given above may therefore be a lower limit for charge transfer from an excited cyanine dye into p-chloranil crystals.

The quantum efficiency of (8) yields, without competing energy transfer, with $k_{\mathrm{F}}=9.1\cdot10^8\ \mathrm{sec}^{-1}$ and $k_{\mathrm{CT}}=1.5\cdot10^9\ \mathrm{sec}^{-1}$ a theoretical value of $\Phi_{\mathrm{CT}}=0.6$, that is within the range of experimental values. The latter were determined by the ratio of the photocurrent densities with the generation rate of excited dyes that is given by the flux of photons I through the semitransparent electrode with a transparency T and the absorbance A of a monolayer of typically 1%, $\Phi_{\mathrm{CT}} = j/IAT$. Usually they are higher and even up to one. Sometimes low values are found, and it is suggested that they are due to dye damage in course of evaporation of the metal electrodes as described above [15a].

4. Discussion

The study of the kinetics of a system involves not only the determination of a reaction rate constant, but also, at least, a discussion of the reaction mechanism and the exclusion of competing reactions.

Energy transfer from the excited dye to the crystal cannot be an efficient process, because the dye's excited singlet state with 2.5 eV (Fig. 7) and its triplet state with ≈ 2 eV [32] are lower than the states of available acceptors within the crystal: there are only n-π^* singlet transitions with a low extinction coefficient of 10^2 cm^{-1} [33] and excitation energies of 2.63 eV and 2.72 eV [34] on the shoulder of a π-π^* transition with 3.04 eV (408 nm) available.

Charge transfer causes the photocurrents. The sensitizing action of the dye is possible from its excited singlet state D^* at 3.4 eV [35] into the conduction band CB of the crystal at 4.3 eV [36] (Figure 7). Figure 10 shows two reaction schemes: The simplified one above describes the straightforward reaction of sensitization with the overall rate constant k_{CT} that has been (Chapt. 3) subject of the preceding investigation. Equation (4), supplemented by the back reaction of recombination, is now

$$\begin{tikzcd} D^* + \mathrm{CA} \arrow[r, "k_{\mathrm{CT}}"] & \mathrm{D}^+ + \mathrm{e}^-_{\mathrm{CA}} \arrow[dl, "k_{\mathrm{R}}"] \\ D + \mathrm{CA} & \end{tikzcd} \qquad (15)$$

and the rate for free carrier formation is

$$\frac{d[\mathrm{e}^-_{\mathrm{CA}}]}{\mathrm{d}t} = k_{\mathrm{CT}}[D^*] - k_{\mathrm{R}}[\mathrm{e}^-_{\mathrm{CA}}] \qquad (16)$$

(throughout the paper surface densities are used). Constant quantities like [CA] and [D$^+$] are drawn together with the relevant rate constant in order to get first order rate constants, e.g. $k_{\mathrm{CT}} = k'_{\mathrm{CT}}[\mathrm{CA}]$ and $k_{\mathrm{R}} = k'_{\mathrm{R}}[\mathrm{D}^+]$.

The extended reaction scheme shown in the lower part of Fig. 10 involves in a microscopic picture of the charge transfer step the intermediate state ($\mathrm{D}^+ \ldots \mathrm{e}^-_{\mathrm{CA}}$) [12, 37], the dissociation of which with k_{es} is now the rate determining step

$$\begin{tikzcd} D^* + \mathrm{CA} \arrow[dr, "k_{\mathrm{d}}"] & & \\ & (\mathrm{D}^+ \ldots \mathrm{e}^-_{\mathrm{CA}}) \arrow[r, shift left, "k_{\mathrm{es}}"] \arrow[dl, "k_{\mathrm{r}}"] & \mathrm{D}^+ + \mathrm{e}^-_{\mathrm{CA}} \,. \arrow[l, shift left, "k_{\mathrm{re}}"] \\ D + \mathrm{CA} & & \end{tikzcd} \qquad (17)$$

Similarly to (16), the rate equation for free carrier formation $d[\mathrm{e}^-_{\mathrm{CA}}]/\mathrm{d}t$ has been derived [38] as well as those for the preceding state, $d[\mathrm{D}^+ \ldots \mathrm{e}^-_{\mathrm{CT}}]/\mathrm{d}t$. Some rearrangement yields finally the photocurrent density in analogy to (1):

$$j = e[k_{\mathrm{d}}[\mathrm{D}^*]\,\Phi_{\mathrm{ES}} - k_{\mathrm{re}}[\mathrm{e}^-_{\mathrm{CA}}](1 - \Phi_{\mathrm{ES}})], \qquad (18)$$

with the quantum efficiency $\Phi_{\mathrm{ES}} = k_{\mathrm{es}}/(k_{\mathrm{es}} + k_{\mathrm{r}})$ for free carrier formation from the intermediate state. The second term vanishes for quantum efficiencies up to one, but it vanishes also under electrode limited current conditions, because in this case $[\mathrm{e}^-_{\mathrm{CA}}] \to 0$. The first term can be compared with (1), and it follows that the overall rate constant k_{CT} is $k_{\mathrm{d}}\,\Phi_{\mathrm{ES}}$.

A further treatment of (1) and (18) requires the calculation of $[D^*]$ via the reaction scheme

$$D + h\nu \underset{k_{\mathrm{F}}}{\overset{\sigma I}{\rightleftharpoons}} D^* \qquad (19)$$

and the rate equation, that has to involve the charge transfer step (k_{CT} for the simplified scheme

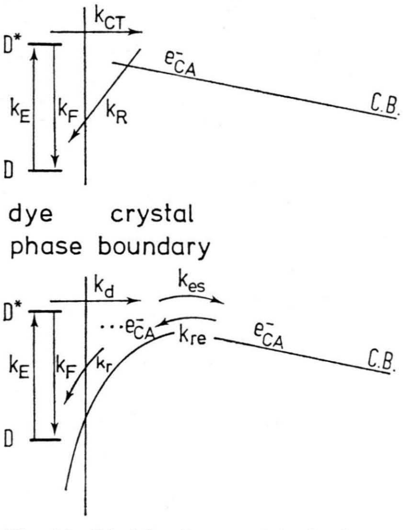

Fig. 10. Models for sensitized charge carrier injection. above: simplified description for the overall process; below: detailed reaction scheme including the intermediate state ($\mathrm{D}^+ \ldots \mathrm{e}^-_{\mathrm{CA}}$).

(Fig. 10, above) and k_{d} for the extended scheme, below),

$$d[D^*]/\mathrm{d}t = \sigma\, I[D] - (k_{\mathrm{F}} + k_{\mathrm{d}})[D^*]\,. \tag{20}$$

It yields under equilibrium conditions

$$[D^*] = \frac{\sigma(\lambda)\, I[D]}{k_{\mathrm{d}} + k_{\mathrm{F}}}\,. \tag{21}$$

Together with (18) the photocurrent density becomes now, in analogy to (5),

$$j = e\,\sigma(\lambda)\, I[D]\, \Phi_{\mathrm{D}}(d) \cdot \Phi_{\mathrm{ES}}\,, \tag{22}$$

and comparison shows $\Phi_{\mathrm{CT}}(d) = \Phi_{\mathrm{D}}(d) \cdot \Phi_{\mathrm{ES}}$, i.e. the measurable over-all quantum efficiency $\Phi_{\mathrm{CT}}(d)$ for the photocurrent is the product of the dissociation efficiency of the excited dye, $\Phi_{\mathrm{D}}(d) = k_{\mathrm{d}}/(k_{\mathrm{d}} + k_{\mathrm{F}})$, times the efficiency for charge carrier escape, $\Phi_{\mathrm{ES}} = k_{\mathrm{es}}/(k_{\mathrm{es}} + k_{\mathrm{r}})$.

Numerical estimations from calibrated measurements are possible on the basis of (1) and (21). It has been stated that (1) is not suitable to calculate k_{CT} because the density of excited dye molecules is not known. Now, as $k_{\mathrm{CT}} = 1.5 \times 10^9\ \mathrm{s}^{-1}$ has been determined by an independent method, (1) is even suitable to determine $[D^*]$. It can be compared with an estimation from (21):

With a typical photocurrent $j = 1.1 \times 10^{-7}\ \mathrm{A\,cm}^{-2}$ and $k_{\mathrm{CT}} = 1.5 \times 10^9\ \mathrm{s}^{-1}$ it follows from (1) that $[D^*] = 4.6 \times 10^2\ \mathrm{cm}^{-2}$. However, insertion into (21) of $\sigma = 1.7 \times 10^{-16}\ \mathrm{cm}^{-2}$, $I = 8 \times 10^{14}$ photons $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ at 496 nm, $[D] = 10^{14}\ \mathrm{cm}^{-2}$ (the actual area of one dye molecule [39] is 75 Å^2, but a tight arrangement cannot be assumed), $k_{\mathrm{d}} \approx k_{\mathrm{CT}} = 1.5 \times 10^9\ \mathrm{s}^{-1}$, and $k_{\mathrm{F}} = 9.1 \times 10^8\ \mathrm{s}^{-1}$ yields $[D^*] = 5.6 \times 10^3\ \mathrm{cm}^{-2}$.

The second estimation yields a value that is about one order of magnitude too high. This suggests that either $[D]$ is far from a tight bricklayer arrangement [39] or the actual dye concentration has been reduced by dye damage in course of preparation [15a].

Finally, the presented results could be a model experiment to explain the decreasing photocurrents with increasing dye concentration for systems like an aqueous solution of rhodamine B [5] or methylene blue [41] on the surface of anthracene crystals. In addition to the proposed aggregated adsorption [40] and hindered access of oxygen [41] it might be suggested on the basis of competing energy transfer that with increasing concentration, and probably enhanced by adsorption phenomena, the interaction radius between the molecules decreases and due to Förster's resonance transfer [42] excitation energy is withdrawn from the surface.

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[1] W. West, in "Dye Sensitization", eds. W. F. Berg, U. Mazzucato, H. Meier, G. Semerano, Focal Press, London 1970, p. 105.

[2] L. v. Szentpály, D. Möbius, and H. Kuhn, J. Chem. Phys. **52**, 4618 (1970).

[3] F. Dörr and G. Scheibe, Z. Wiss. Phot. **55**, 133 (1961). R. C. Nelson, J. phys. Chem. **71**, 771 (1967).

[4] a) H. Gerischer, Photochem. Photobiol. **16**, 243 (1972). b) H. Gerischer and H. L. Selzle, Electrochim. Acta **18**, 799 (1973).

[5] H. Kallmann and M. Pope, J. Chem. Phys. **32**, 300 (1960).

[6] J. W. Steketee and J. de Jonge, Proc. Kon. Ned. Akad. Wet. Ser. B **66**, 76 (1963); B. J. Mulder and J. de Jonge, ibid., Ser. B **66**, 303 (1963).

[7] R. Matejec and J. Nys, in: "Dye Sensitization", eds. U. F. Berg, U. Mazzucato, H. Meier, G. Semerano, Focal Press, London 1970.

[8] a) H. Meier, "Spectral Sensitization", Focal Press, London 1968, p. 83. b) J. Bourdon and B. Schnuriger, in: "Physics and Chemistry of the Organic Solid State", eds. D. Fox, M. M. Labes, and A. Weissberger, Vol. 3, p. 60, Interscience, New York 1967.

[9] H. Killesreiter, J. Lumin. **12/13**, 857 (1976).

[10] Fluorescence measurements and their consideration similar to Ref. [2] in calculating the rate constant have been proposed by H. Kuhn and D. Möbius.

[11] a) H. Killesreiter, Faraday Disc. Chem. Soc. **58**, 271 (1975). b) H. Killesreiter, Ber. Bunsenges. Phys. Chem. **82**, 503, 512 (1978).

[12] R. Haberkorn, W. Harengel, H.-P. Braun, and M. E. Michel-Beyerle, Ber. Bunsenges. physik. Chem. **77**, 928 (1973).

[13] J. Sondermann, Liebigs Ann. Chem. **794**, 183 (1971).

[14] a) H. Bücher, K. H. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F. P. Schäfer, J. Sondermann, W. Sperling, P. Tillmann, and J. Wiegand, Mol. Cryst. **2**, 199 (1967). b) H. Kuhn, D. Möbius, and H. Bücher, in "Physical Methods of Chemistry" I, 3B, eds. A. Weissberger and B. Rossiter; John Wiley and Sons Inc., New York 1972.

[15] a) Similarly to a bathochromic shift that can be observed in the absorbance of dye monolayers on a glass slide for an increasing mole ratio of dye/arachidic acid, a destruction of dye molecules in the sandwich cells is not only indicated by an apparent lower quantum efficiency of the photocurrent, but also by a hypsochromic shift in the action spectra, thus making them to a spectroscopy of the interaction of adsorbed dye molecules (details in preparation). b) From H. Schopper, Metalle und Legierungen, in: Landolt-Börnstein, Zahlenwerte und Funktionen, Eds. K.-H. Hellwege and A. M. Hellwege, Optical Constants, Vol. II, Part 8, Springer-Verlag, Berlin 1969, we get for the absorption constant $K = 4\pi k/\lambda_V = 1.32 \times 10^{-2}$ Å^{-1} with $k = 5.19$ at a wavelength in vacuo of $\lambda_V = 4916$ Å for an evaporated aluminum layer. From the transparency T of a layer with thickness x[Å] follows from $T = I(x)/I(0) = \exp(-Kx) = 0.2$ a layer thickness of $x = 1.21 \times 10^2$ Å. The actual film thickness may be larger, because this calculation does not account for inhomogeneities that are not only due to the formation of an Al_2O_3-layer (Ref. [19]) but also due to discontinuous formation of metal crystallites or patches. More details are given in: J. W. Geus, Fundamental Concepts in Film Formation, in: Chemisorption and Reactions in Metallic Films, Ed. J. R. Anderson, Academic Press, London 1971, Vol. I, p. 129.

[16] The fluorescence apparatus has been designed and built by H.-D. Försterling and H. Schreiber in a modified version of that described in Ref. [14b].

[17] H. Kuhn, J. Chem. Phys. **53**, 101 (1970).

[18] O. Inacker and H. Kuhn, Chem. Phys. Letters **27**, 317 (1974).

[19] P. H. Berning, G. Hass, and R. P. Madden, J. Opt. Soc. Amer. **50**, 586 (1960).

[20] R. R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. **62**, 2245 (1975); **65**, 2527 (1976); **66**, 1765 (1977).

[21] a) G. Vaubel, H. Bässler, and D. Möbius, Chem. Phys. Lett. **10**, 334 (1971). b) H. Kurczewska and H. Bässler, J. Lumin. **15**, 261 (1977). c) H. Kallmann, G. Vaubel, and H. Bässler, Phys. Stat. Sol. (b) **44**, 813 (1971).

[22] H. Morawitz and M. R. Philpott, Phys. Rev. B **10**, 4863 (1974).

[23] J. Dexter, J. Chem. Phys. **21**, 836 (1953).

[24] H. Killesreiter and H. Bässler, Phys. Stat. Sol. (b) **51**, 657 (1972).

[25] M. Lampert and P. Mark, Current Injection in Solids, Academic Press, New York 1970. W. Helfrich, in: Physics and Chemistry of the Organic Solid State, III, Eds. D. Fox, M. M. Labes, and A. Weissberger, Intersci. Publ., New York 1967.

[26] a) N. E. Geacintov and M. Pope, Proc. 3rd Int. Photocond. Conf., Stanford 1969, ed. E. M. Pell (Pergamon Press 1970). b) H. Killesreiter and H. Bässler, phys. Stat. Sol. (b) **53**, 193 (1972). c) J. S. Bonham and L. E. Lyons, Aust. J. Chem. **26**, 489 (1973). d) H. Killesreiter, VIIIth Molecular Crystal Symposium, Santa Barbara, Calif., 1977; details to be published.

[27] H. Killesreiter, Ber. Bunsenges. physik. Chem. **77**, 938 (1973).

[28] H. Killesreiter and S. Schneider, Chem. Phys. Lett. **52**, 191 (1977).

[29] B. Mann and H. Kuhn, J. Appl. Phys. **42**, 4398 (1971).

[30] a) P. J. Reucroft and W. H. Simpson, Faraday Disc. Chem. Soc. **51**, 202 (1971). b) M. Sugi, K. Nembach, D. Möbius, and H. Kuhn, Solid State Commun. **15**, 1867 (1974).

[31] M. Hauser measured by picosecond sampling technique the fluorescence decay time of the dye in monolayer arrangement on a glass slide $\tau = 1/k_F = 1.3 \times 10^{-9}$ sec. At the VIIIth Molecular Cryst. Symposium, Santa Barbara 1977, $k_{CT} = (1.6 \pm 0.8) \cdot 10^9$ s^{-1}, based on the usually assumed value $k_F = 10^9$ s^{-1} has been presented.

[32] $E_T \approx 2$ eV has been estimated in analogy to the $T_1 - S_0$ transition of the similar dye 3,3′-diethylthiacarbocyanine, published in Ref. [1], p. 131.

[33] P. J. Reucroft, O. N. Rudyj, R. E. Salomon, and M. M. Labes, J. Chem. Phys. **43**, 767 (1965).

[34] H. P. Trommsdorff, J. Chem. Phys. **56**, 5358 (1972).

[35] G. Scheibe and F. Dörr, in Scientific Photography, ed. H. Sauvenier, Pergamon, New York 1962; so-called "Scheibe's rule".

[36] M. E. Michel-Beyerle and F. Willig, Solid State Commun. **7**, 913 (1969).

[37] B. Nickel, Mol. Cryst. Liq. Cryst. **18**, 227 (1972).

[38] H. Killesreiter, Z. Naturforsch. **33a**, 822 (1978).

[39] V. Czikkely, H. D. Försterling, and H. Kuhn, Chem. Phys. Letters **6**, 11 (1970).

[40] H. Killesreiter, submitted for publication.

[41] M. E. Michel-Beyerle and F. Willig, Chem. Phys. Letters **5**, 281 (1970).

[42] Th. Förster, Fluoreszenz organischer Verbindungen, Vandenhoeck und Rupprecht, Göttingen 1951.